

NASA TECHNICAL NOTE



NASA TN D-8177

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APOLLO EXPERIENCE REPORT - DETECTION
AND MINIMIZATION OF IGNITION HAZARDS
FROM WATER/GLYCOL CONTAMINATION OF
SILVER-CLAD ELECTRICAL CIRCUITRY

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1. Report No. NASA TN D-8177		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle APOLLO EXPERIENCE REPORT: DETECTION AND MINIMIZATION OF IGNITION HAZARDS FROM WATER/GLYCOL CONTAMINATION OF SILVER-CLAD ELECTRICAL CIRCUITRY				5. Report Date March 1976	
				6. Performing Organization Code JSC-09911	
7. Author(s) W. Richard Downs				8. Performing Organization Report No. JSC S-449	
				10. Work Unit No. 986-15-31-01-72	
9. Performing Organization Name and Address Lyndon B. Johnson Space Center Houston, Texas 77058				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Note	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract The potential flammability hazard when a water/glycol solution contacts defectively insulated silver-clad copper circuitry or electrical components carrying a direct current is described. The chemical reactions and means for detecting them are explained. Methods for detecting and cleaning contaminated areas and the use of inhibitors to arrest chemical reactivity are also explained.					
17. Key Words (Suggested by Author(s)) * Flammability * Coolants * Corrosion Prevention * Inhibitors * Fire Prevention * Chemical Attack * Additives * Deicer Fluids * Insulation * Circuitry				18. Distribution Statement STAR Subject Category: 12 (Astronautics, General)	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		22. Price* \$3.25	
				21. No. of Pages 20	

APOLLO EXPERIENCE REPORT

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DETECTION AND MINIMIZATION OF IGNITION HAZARDS FROM
WATER/GLYCOL CONTAMINATION OF SILVER-CLAD ELECTRICAL CIRCUITRY

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SUMMARY

Following the Apollo-Saturn 204 incident in January 1967, it was discovered in laboratory work that bare or defectively insulated silver-clad copper wires carrying a direct-current potential produced ignition, evidenced by a small self-sustaining flame, when contacted by water/glycol fluids.

Mechanisms for inhibiting water/glycol-induced reactions with metals were investigated with particular reference to the Apollo coolant fluids. Measurements of milli-ampere current flow during the reaction of water/glycol with silver and the utilization of a transistorized amplitude-modulation receiver for detecting radiofrequency emissions were found effective as a means of locating circuitry defects leading to flame production.

Because water/glycol coolant fluids cannot easily be removed from contaminated circuitry, use of a silver chelating agent in the water/glycol coolant to arrest chemical reactivity and thereby minimize the hazards of flammability was proposed. When spillage of water/glycol occurs on electrical equipment, the circuit elements must be washed and the parts tested for freedom from contamination before the system can be qualified as hazard free. Techniques for flushing electrical circuitry as a part of quality assurance procedures are described.

INTRODUCTION

Since World War II, silver-clad copper wires (Military Specifications MIL-W-7139 and MIL-W-8777) have been used in electrical circuits in military aircraft because of the ease and reliability with which silver (Ag) can be soldered to produce high-quality electric circuits. Consequently, spacecraft engineers and builders specified silver-clad copper wires in spacecraft construction. Use of silver-clad wires, switches, and disconnects seemed sound, not only because of the ease of joining but also because of the protection afforded copper by the resistance of silver to oxidation when high-melting polymers for electrical insulation coverings were extruded over the

conductor. Because of occasional bleedthrough of copper to the surface of the silver and for mechanical strength, some aerospace designers specify nickel-covered copper wires instead of silver-clad copper wires. The ground-support-equipment wiring and auxiliary wiring are usually insulated and are composed of pure copper or tin-plated copper.

Solutions of ethylene glycol and water (called water/glycol) have been used in cooling systems of land and amphibious vehicles, in the thermal transport systems of aircraft and spacecraft, and as a deicer fluid for aircraft for many years. Water/glycol solutions are used in a variety of applications because of the high heat capacity, the relatively nontoxic components, the exceptional properties at low temperatures, and the low pumping pressures and flow rates over the operating thermal range of the radiator system. Because they have low solidification temperatures, low vapor pressures, and low viscosities as a function of temperature, water/glycol solutions are also excellent deicer agents for preventing and removing frost and ice from most surfaces.

When mixed with water, ethylene glycol lowers the freezing point and raises the boiling point of the mixture without significantly affecting its specific heat. Water/glycol solutions, therefore, are efficient thermal transport fluids for closed-loop systems and are used in the aerospace and automotive industries as deicer agents. Except for instances of corrosive action on metals, the chemical reactivity of water/glycol solutions was not fully recognized until after the Apollo-Saturn 204 fire in 1967 when studies were made at the NASA Lyndon B. Johnson Space Center (JSC) (formerly the Manned Spacecraft Center (MSC)) to determine the possible hazardous characteristics of water/glycol. These studies led to the disclosure that ethylene glycol solutions in contact with silver wire circuitry carrying direct current react chemically to produce ignition; if the reacting solution is left undisturbed, the flammability is self-sustaining as long as glycol fluid is present.

During the laboratory investigations, it was observed that a defectively insulated spacecraft coaxial silver-clad copper cable carrying 28 volts direct current in a 115-kN/m^2 (16.7 psia) pure oxygen atmosphere resulted in a small self-sustaining flame when water/glycol thermal transport fluids dripped over the cables. The time required to attain ignition after onset of the water/glycol exposure was an inverse function of the drip rate; that is, the slower the drip rate, the more rapidly ignition occurred. Further observation showed that defectively insulated pure copper cables exposed to water/glycol coolant in oxygen did not necessarily produce fire.

An examination was made of the water/glycol-induced corrosion of metals, of the mechanisms for inhibiting corrosion, and of the reasons why silver-clad copper wires reacted differently than pure copper or nickel-covered copper wires when exposed to water/glycol solutions. This report discusses the use of additive reagents found effective in inhibiting reactivity of water/glycol solutions on wire circuitry, the means of detecting chemically induced ignition hazards of glycol fluids in the Apollo systems, and the methods recommended for minimizing these hazards.

The objectives of this Apollo experience report are to delineate chemically induced ignition hazards of glycol solutions resulting from spillages and leakages, to describe methods of detecting these hazards, and to show what can be accomplished to minimize them.

As an aid to the reader, where necessary the original units of measure have been converted to the equivalent value in the Système International d'Unités (SI). The SI units are written first, and the original units are written parenthetically thereafter.

INHIBITING FLUID-METAL REACTIONS

In the presence of air or oxygen (O_2) at ambient or higher temperatures, ethylene glycol in solution tends to oxidize to glycolic acid, and the mixture becomes more and more corrosive to aluminum alloys in contact with the solution. Once corrosion starts, the rate of attack increases rapidly, and the effects of corrosion become increasingly serious. A number of inhibitors, however, can be added to reduce the rate of corrosion of metals. One common inhibitor is a mixture of phosphate and potassium tetraborate, another is boric acid, and another - especially suitable for aluminum alloy systems - is a mixture of triethanolamine phosphate (TEAP), a pH buffering agent, and sodium mercaptobenzothiazole (NACAP), a copper chelating agent.

The inhibitor system found superior for the Apollo spacecraft environmental control units was termed "NAA Type II" and consisted of TEAP and NACAP. The TEAP in NAA Type II has three functions: (1) to draw copper atoms from the surface of the alloy into solution, allowing the chelating agent (NACAP) to react with the copper ions to form an undissociated copper chelate (organometallic complex); (2) to supply phosphate ions to produce a uniform coating of aluminum phosphate over the metal surfaces, thereby protecting the natural oxide coating; and (3) to serve as a phosphate salt buffer for maintaining the hydrogen-ion concentration of the solution at approximately pH 7 and preventing wide local excursions of the hydrogen-ion concentration.

The choice of an inhibitor system for water/glycol solutions depends on the metals used in the coolant loop construction. The Apollo environmental control system utilized NAA Type II in a eutectic mixture (a mixture that has the lowest freezing point possible) of 62 percent ethylene glycol and 38 percent water. This mixture carries the trade name "RS 89-a."¹ The RS 89-a mixture is not a fire hazard in a 103-kN/m² (15 psia) oxygen atmosphere, in which its autoignition temperature was demonstrated to be higher than 505 K (450° F); in air, this point was 694 K (790° F) for RS 89-a and 672 K (750° F) for pure ethylene glycol. The flashpoint temperature of RS 89-a is between 383 and 389 K (230° and 240° F).

¹RS 89-a is compounded to the following proportions: 566 grams of ethylene glycol, 339.5 grams of distilled water, 14.18 grams of TEAP, and 1.41 grams of NACAP (50-percent solution) for a total of 921.09 grams.

Certain properties of inhibited water/glycol solutions contribute to the hazards of flammability and complicate cleanup procedures when these solutions contact electrical circuitry. Such properties are the high conductance of glycol solutions and the low vapor pressures imparted by the ethylene glycol constituent. The RS 89-a mixture, for example, yields an ionic concentration of approximately 243 p/m at 296 K (23° C); laboratory-distilled water yields 0.5 to 1.0 p/m at 296 K (23° C). This means that the solution will readily conduct electricity, and material transport will then occur between oppositely charged conductors exposed in the solution. Because ethylene glycol has a low vapor pressure at room temperature, it is impractical to remove water/glycol solutions from contaminated surfaces by evaporative processes.

CLEANING UP SPILLS

A series of laboratory experiments was performed at MSC to determine the physical properties of RS 89-a and its effects on wire circuitry so that a method could be specified for cleaning contaminated circuit elements. The laboratory distilled water at ambient temperature (296 K (23° C)) has an ion concentration of approximately 0.74 p/m. By contrast, RS 89-a fluid at ambient temperature produces an ion concentration of 243 p/m because of the phosphate and sodium ions in the inhibitors.

The RS 89-a mixture cannot, within practical time limits, be completely evaporated by vacuum techniques because of the presence of the ions and because of the low vapor pressures of the ethylene glycol and undissociated amines. Excess tertiary amine and its phosphate, on evaporation of the solvent, remain as hygroscopic material and are deliquescent. They tend to attract moisture from the surroundings to produce an electrically conductive, corrosive fluid. The sodium ions present will remain as the salt sodium mercaptobenzothiazole. The sodium ions, the undissociated alkaline amine, and the ethylene glycol remain when RS 89-a is spilled around electrical cables or onto electrical connectors, despite efforts to evaporate the spillage by drawing a vacuum.

Flammability hazards are induced by the chemical reactivity of water/glycol solutions with silver wire circuitry because of accidental spillage or leakage onto defective electrical wire insulation or an incorrectly designed wire harness. If a practical means of detecting glycol contamination were established to identify possible reaction sites and if a procedure were established for minimizing the effects of contamination, flammability hazards induced by the chemical reactivity of water/glycol solutions with silver circuitry could be substantially reduced.

DETECTING CHEMICAL REACTIONS

The chemical reactivity of ethylene glycol with silver wire circuitry can be observed in several ways, primarily in the production of smoke, pungent odors, and flame. Flame production is self-sustaining as long as glycol solution is present to fuel the fire.

Another means of detecting chemical reactivity is the detection of radiofrequency (rf) static disturbances produced on an amplitude-modulation (AM) receiver placed near the defective circuit where reaction is occurring. This detection method seemed sufficiently important to justify an investigation of the phenomenon of this technique.

Tests were conducted to determine the nature of the rf disturbances produced from voltage used on spacecraft. A silver-shielded twisted pair of insulated silver-clad copper wires was used in the tests. This specimen was nicked through the shield and also through the insulation of the two center conductors so that the center conductors were exposed near the shield. On one end of the test sample, the two center wires were tied together and then attached to one terminal of a voltage source; the shield was tied to the other terminal of the voltage source. The RS 89-a mixture was allowed to drip onto the defect in the shield and through the insulation.

The tests indicated that the electrochemical reactions produced a broadband rf noise (14 kilohertz to 30 megahertz) and that the rf intensity generated by the reactions varied irregularly with time. This time variation was found to be an inherent characteristic of the reactions. Most of the noise intensities were too low for accurate measurements. However, only short wire specimens (several centimeters) were tested; if longer wire lengths (approaching the lengths used in aircraft and spacecraft circuits) had been tested, it is believed that a significant increase in radiated levels would have resulted. A characteristic unique to the rf disturbance is the slow buildup of amplitude with time. During electrical checkout of a spacecraft or aircraft electrical system, the background noise levels might mask the rf disturbances. For this reason, if measurements of rf disturbances are made as a means of detecting incipient hazards, the measurements should be performed on single-powered circuits.

A third method of detecting chemical reactivity is to observe the current flow in an open circuit as the chemical reactions commence and are maintained. Tests were conducted in an oxygen atmosphere on silver-clad coaxial cables in which a defect was produced by grinding a groove to expose the center conductor. The test fluid (RS 89-a) was dripped onto the defect at a rate of one drop every 5 minutes. A potential of 28 volts direct current was applied across the cable, and the current

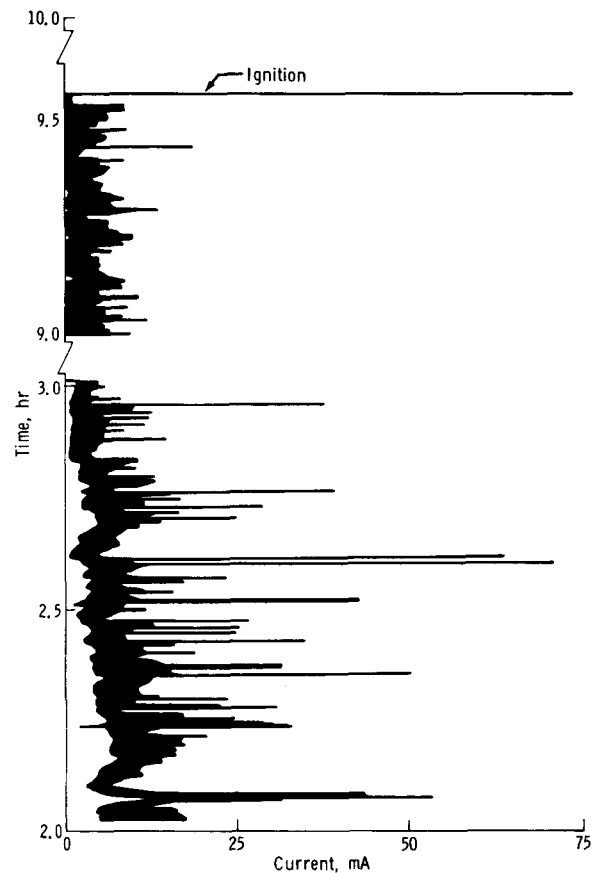


Figure 1. - Recorder trace of currents produced when water/glycol solution contacts silver-clad wires carrying 28 volts direct current.

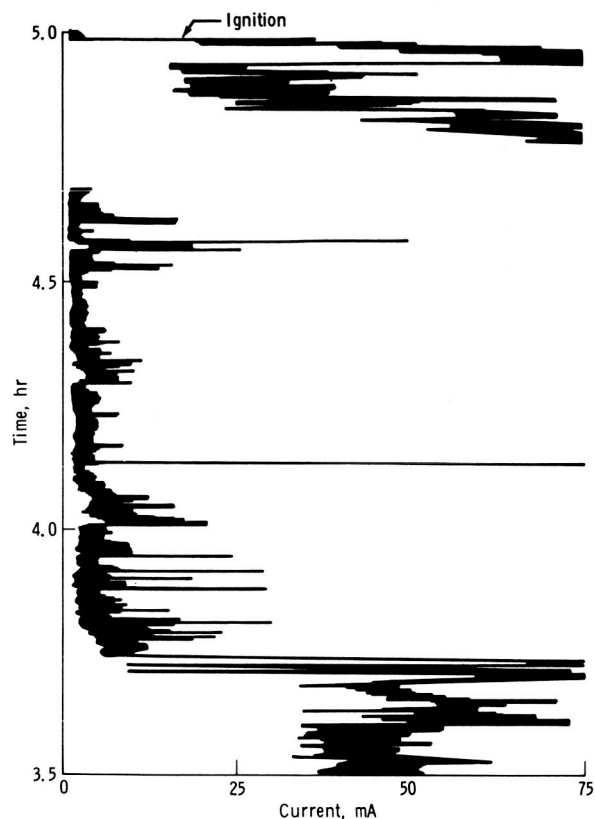


Figure 2. - Recorder trace of currents produced when RS 89-a solution contacts silver-clad wires carrying 28 volts direct current.

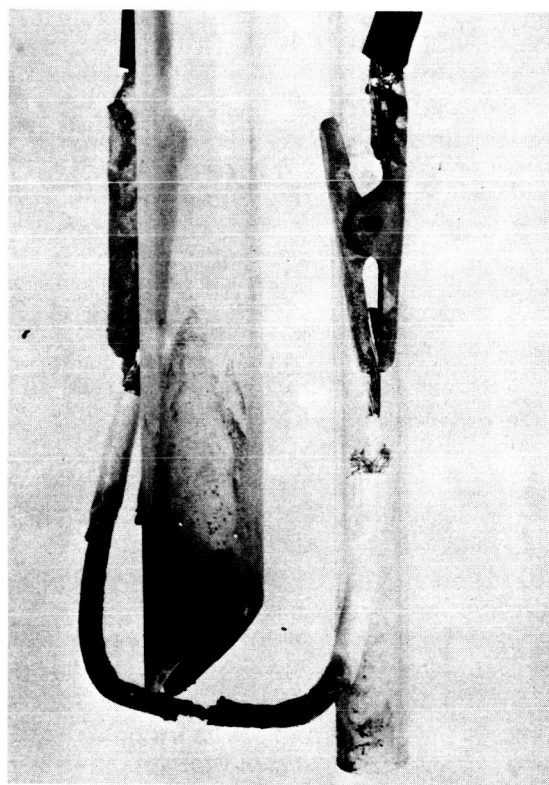


Figure 3. - Specimen of silver-clad coaxial cable carrying 28 volts direct current after RS 89-a was dripped on defect in insulation. The burned condition of the cable is shown.

flow was recorded. The current was highly irregular and was much larger than would be expected on the basis of the solution conductivity alone. Typical portions of the recorder traces for the cable tests conducted with RS 89-a are shown in figures 1 and 2. Ignition occurred between 9 and 10 hours when the water/glycol fluid was used and at approximately 5 hours when the RS 89-a solution was tested. Figure 3 shows the burned condition of the cable after the test with RS 89-a.

Because of the hygroscopic nature of the amine residues and the existence of ions, a corrosive, electrically conductive moist locale is produced, commencing with the admission of air or moist oxygen to equipment soaked in RS 89-a. The attraction of moisture to regions stained with RS 89-a is time dependent and cumulative.

TEST RESULTS

Observations showed that bare or defectively insulated silver-clad copper wires (carrying a direct-current potential) exposed to water/glycol solutions produced smoke

and fire in oxygen or in air. Also, it was found that pure copper wires or nickel-covered copper wires under conditions of electrical potential and oxygen exposure identical to those of silver-clad wires did not exhibit chemical reactivity to water/glycol solutions and did not produce ignition.²

Silver-clad copper wire was completely stripped of its insulation. Two pieces, each about 5 centimeters long, were taped to cardboard so that approximately a 1-millimeter space separated the two wires. A 22.5-volt dry-cell battery supplied direct current, and a milliammeter was placed in series. The RS 89-a solution was dripped slowly into the 1-millimeter space between the wires. Electrolysis began immediately; in 4 to 5 seconds, a black deposit was observed on the silver wire connected to the positive terminal of the battery. The milliamperage current flow fluctuated between 10 and 80 milliamperes, and the needle of the meter fluctuated constantly. In a few minutes, copious white smoke and flame ensued. These phenomena occurred whether the reaction was carried out in air or in 100-percent oxygen at 103 kN/m² (15 psia).

A transistorized AM receiver (covering the commercial broadcast band from 600 to 1400 kilohertz) placed near the electrolysis started to click and emit static, which, as the electrolysis proceeded, built up to a constant static noise that drowned out all other reception on the receiver. The rf disturbance was observed on the receiver when it was held as far away as 1 meter (3 feet), and the intensity of the noise increased as the receiver was moved toward the reaction site. The application of the AM receiver to detect a reaction between the water/glycol solution and the silver wiring was found to be more convenient than using a milliammeter in the circuit. The slower the application of water/glycol solution after the first drop or two, the louder the rf disturbance over the receiver became. Eventually, the chemical reactions detected by the AM receiver produced smoke and flame.

Nickel-covered copper wires, pure copper wires, and tin-plated copper wires did not show evidence of chemical reactivity when subjected to a direct-current potential and exposed to the water/glycol solution. In such instances, the solution simply electrolyzed with mild generation of heat, with no rf radiation emission, and with no tendency to flammability.

It makes little difference in reactivity whether the water/glycol fluid is simply ethylene glycol solution in water or whether the fluid contains inhibitors such as NAA Type II or Type III. Chemical reaction of silver with water/glycol solution occurs only when the silver is connected to the positive terminal. This signifies that the silver undergoes anodic oxidation, which occurs readily at a 6-volt potential but is barely apparent at a 1.55-volt potential.

²D. K. Elliot (ref. 1) reports on so-called wet-wire fires produced from insulated wires of various metal compositions when the wires are exposed to direct current and to aqueous conducting solutions. The work of Elliot discusses a different sort of phenomenon, the formation of metallic dendrites leading to an electrical short circuit, followed by ignition and burning of the wire insulation.

Reaction occurs as soon as water/glycol contacts the current-carrying silver-clad wires and is indicated initially by electrolysis between the wires and by the formation of a black deposit. Steps in the chemical mechanism leading to ignition are shown in figures 4 to 8. These figures are stereoscopic photomicrographs produced from frames of a motion picture of the reaction resulting when RS 89-a fluid was placed between two silver-clad wires separated by a distance of 1 millimeter and impressed with 22.5 volts of direct current. The action occurred over a span of approximately 1 minute, during which the current did not exceed 80 milliamperes and the average current was 50 milliamperes. In the photographs, the upper wire is negative and the lower wire is positive.

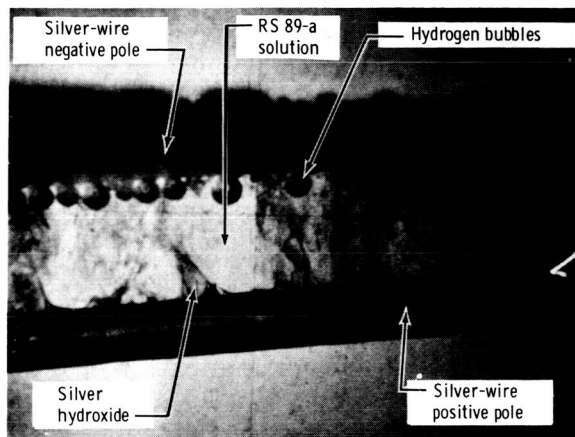


Figure 4. - Photomicrograph of formation of silver hydroxide and hydrogen when a water/glycol solution first contacts silver-clad copper wires.

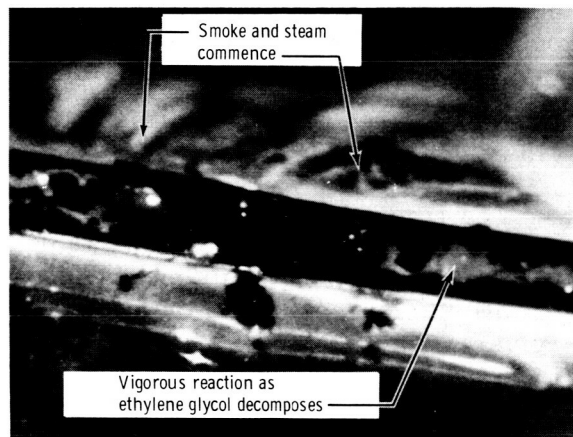


Figure 6. - Photomicrograph of initiation of smoke and steam and a region of massive dehydration of ethylene glycol to form ethylene oxide and ethylene.

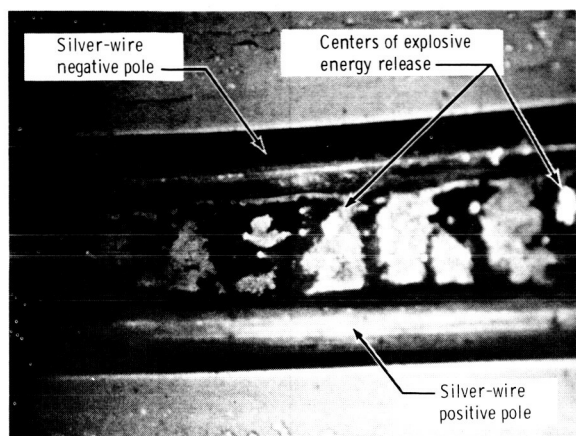


Figure 5. - Photomicrograph of conglomeration of silver oxide in which centers of explosive energy release can be seen.

Figure 4 shows hydrogen (H_2) bubbles forming at the negative pole and streamers of brown silver hydroxide ($AgOH$) issuing from the positive pole. This reaction occurred as soon as the current was impressed.

As seen in figure 5, within a few seconds, the silver hydroxide conglomerated to black silver oxide (Ag_2O). Centers of explosive energy releases are visible in the mass of silver oxide as ethylene glycol commenced to dehydrate.

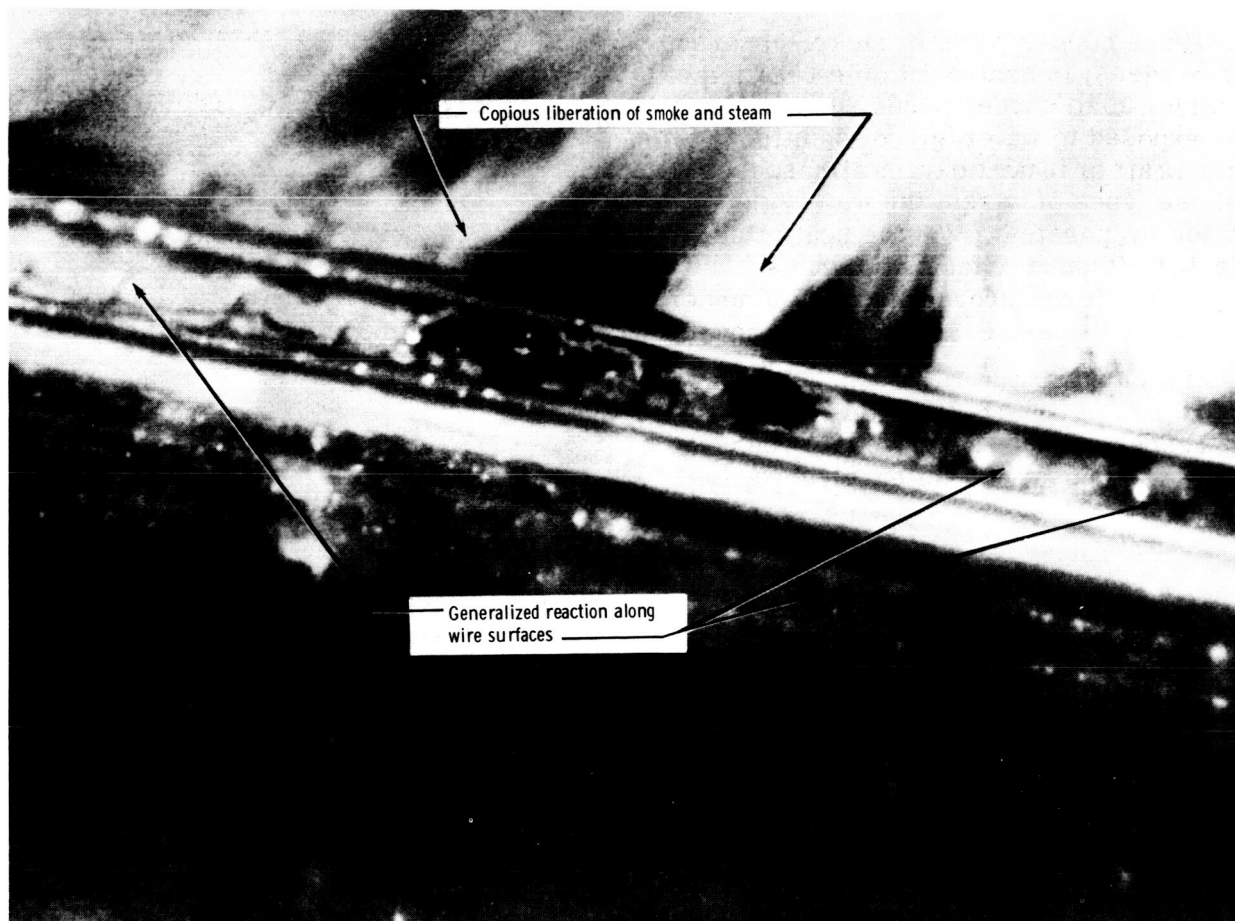


Figure 7. - Photomicrograph of copious liberation of steam and generalized decomposition of ethylene glycol along the wire surfaces.

Figure 6, a view taken several seconds after the view in figure 5, shows an extensive region of glycol oxidation (indicated by an intense blue light) accompanying the decomposition of the ethylene glycol, the rearrangement to form ethylene oxide, and the formation of ethylene. Steam and smoke are observed rising from the negative-pole regions.

Figure 7 shows generalized reaction all along the wire surfaces and copious liberation of smoke and steam, indicative of energy releases in excess of the energy drain from the battery. The total power from the battery, if the maximum current rate were maintained for 1 minute, would be 108 joules (approximately 26 gram-calories), sufficient to produce silver oxide and hydrogen, as noted in figures 4 and 5.

In figure 8, a burst of flame, caused by the reactions of ethylene oxide with hydrogen and of ethylene with air, is visible in the negative-pole region. Another burst is seen at the right side. Analysis showed that the washed and dried black deposit contained silver, carbon, oxygen, and nitrogen.

Pure copper wires or nickel-covered copper wires, in contrast to the reaction of the silver-clad copper wires, do not react when exposed to water/glycol solutions, either in air or in pure oxygen atmospheres. On these types of wires, the water/glycol solution evaporates (from the heat of electrolysis) without producing incandescence or sparks. It has proved impossible under the test conditions, even in a 100-percent oxygen atmosphere at 103 kN/m^2 (15 psia), to produce ignition from nickel-covered or pure copper wires carrying direct-current voltage on exposure to water/glycol solutions.

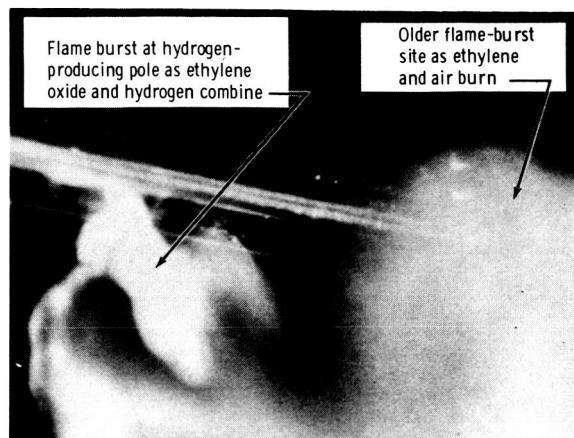


Figure 8. - Photomicrograph of a burst of flame at the wire surface of the negative pole caused by ignition of ethylene oxide and hydrogen and of ethylene with oxygen in air.

CHEMICAL REACTION AND PREVENTION

A chain-reaction mechanism involving the action of water/glycol solution on silver wire begins with the anodic reactions



The chain-reaction mechanism may be prevented if a silver chelating agent exists in a solution to immobilize the Ag^+ ion before it can form silver oxide. Such a chelating agent is benzotriazole (BZT). It was experimentally confirmed that BZT in concentrations of 2000 to 5000 p/m in water/glycol solutions inhibits the chemical reactions of silver and glycol under an impressed direct-current potential. No black deposits form on the silver electrode, no rf radiation is detectable on an AM receiver near the reaction site, the reactants do not tend to flame, and the current flow is steady and decreases with time. The interaction of BZT decreases the activity of silver toward water/glycol solutions to a point at which the silver-clad copper wires behave similarly to nickel-covered or pure copper wires; that is, a simple electrolysis

occurs between the short-circuited wires and gradually ceases as the solution evaporates. The BZT interaction produces a greenish-white, gelatinous precipitate around the silver conductors. This precipitate presumably is an organosilver chelate hydroxide that removes the silver ion and thereby prevents formation of silver oxide. The current flow between the wires is impeded by the precipitate, and the reaction rates are noticeably slowed. The chain reaction leading to flammability is interrupted and prevented.

MINIMIZING HAZARDS

Once contamination of electrical circuits occurs, the effects should be minimized by removing the contaminant and cleaning up the circuitry or by using water/glycol fluids containing a chemical chelating agent that is capable of breaking the chain reaction of ethylene glycol with silver.

General Procedures for Removing Glycol Contamination

The source of glycol spillage must be located and promptly corrected. Runoff of glycol from the spillage site must be prevented. Personnel activities in the spillage area must be minimized.

Once spillage or leakage of glycol solution has occurred, the contamination should be cleaned up at once by proceeding as follows.

1. Estimate the amount of spillage and determine the regions contaminated.
2. Follow an orderly sequence of equipment cleaning, concentrating first on electrical wiring, then on exterior surfaces of black boxes, and finally on plumbing and structural components.
3. Disassemble the equipment and wire bundles.
4. Execute specific cleaning procedures.
5. Verify that all glycol contamination has been removed from contaminated areas.

Detailed Cleanup Procedures

As construction of the Apollo modules (command and service modules and lunar modules) progressed in the Apollo Program, spillages and leakages of water/glycol fluid were encountered from time to time. It was necessary to clean the spacecraft thoroughly after each such incident in a manner that would not jeopardize the quality assurance criteria of spacecraft components or of the spacecraft. The procedures described in subsequent paragraphs were evolved and were applied successfully to water/glycol cleanup of lunar modules LTA-8 and LM-5 and of command and service module 2TV-1.

Electrical components. - The first step in the cleanup of electrical components was to wipe excess glycol solution from wires, black boxes, or structures using clean, dry cloths. For wire bundles and harnesses, the tapes or ties were removed, and all chafe guards were set aside at least 15 centimeters (6 inches) beyond the contaminated region. Cable bundles were cleaned in separate 46-centimeter (18 inch) sections. Each cleaned section overlapped the preceding section by a minimum of 10 centimeters (4 inches). Each wire was wiped individually at least three times with a cloth dampened with distilled water. (The ion content of the water did not exceed 2 p/m.) The wiped wire was then rinsed with distilled water dispensed with a jet-type spray bottle, and the rinse fluid was caught in a container for measurement of ionic concentration. The flow of water was directed over all surfaces being cleaned. Care was taken to ensure that the rinse fluid did not drip, run, or splash, except into the catch container. After the flushing was repeated, the wires were dried using a clean wiper. The dry wires were cleansed using an applicator moistened with isopropyl alcohol and were then wiped with precision cleaning fluid (e.g., Freon TF). (Flushing with solvent and use of solvent on connectors were not permitted.) After cleansing, the wires and connectors were dried using dry nitrogen gas heated to 322 to 344 K (49° to 71° C). The warm nitrogen gas was carefully directed over the wire cables to avoid damaging any part of the assembly. The clean wire harness was then reassembled.

Black boxes. - Cleaning up glycol spillage on exteriors of black boxes included (1) wiping excess fluid from the surfaces of the boxes, from joints and overlaps in the boxes, and from points of ingress to the boxes; (2) wiping the black-box surfaces with cloths moistened with isopropyl alcohol; and (3) drying each surface.

Fixtures and structures. - Cleanup of glycol solution from plumbing fixtures or structural elements included removal of excess spillage with wiper cloths, final cleaning with wiper cloths moistened with isopropyl alcohol, and drying.

Cleanliness Verification

It is important, in the case of silver-clad electrical components, to remove every trace of contamination. Contamination removal, as previously described, was accomplished by rinsing the components with jets of distilled water. After use, the rinse water must be tested for the efficacy of the rinsing process by measuring the ionic concentration in the rinse water with a conductance-measuring instrument. Alternatively, by using a method involving chemical spot checking, the cleanliness of the components can be determined. These methods of testing the rinsing technique are described in subsequent paragraphs.

The presence of ionic contamination is easily determined by use of a conductance-measuring instrument. Solution conductivity is proportional to the ionic concentration. The temperature of the solution being tested must be determined, and the instrument must be compensated for temperature. The ion content of a sample of distilled water is measured; an acceptable level for a supply of distilled water is 2.0 p/m at room temperature. The same procedure is repeated using approximately 100 cubic centimeters of rinse solution. Rinsing should be continued until the rinse water tests no more than 2 p/m over that of the distilled water (a total of 4 p/m).

The chemical spot-check method for verifying cleanliness is as sensitive as conductivity measurements, but it is more difficult to perform. For this test, a piece of filter paper is moistened with distilled water and wiped over the area to be checked for residual glycol contamination. The filter paper is then treated with drops of a chemical solution. The paper contains an indicator that turns blue or violet if glycol is present on the filter paper. (See the appendix for the detailed chemical procedures.)

CONCLUSIONS

Experiments at the NASA Lyndon B. Johnson Space Center (formerly the Manned Spacecraft Center) and NASA-sponsored contract work following the Apollo-Saturn 204 accident in January 1967 demonstrated that bare or defectively insulated silver-clad copper wires carrying direct current could produce ignition when contacted by water/glycol solutions. This phenomenon constitutes a distinct hazard of flammability (wherever ethylene glycol solutions for heat transfer or deicer purposes are used around silver-clad electrical circuitry). Hazards from chemically induced ignition can be detected by noticing the following.

1. Presence of smoke, pungent odors, or flame
2. Radiofrequency static on an amplitude-modulation receiver placed near the electrical circuit defect
3. Microampere currents and their fluctuations in the wiring circuit as determined by a sensitive microammeter mounted in series in the circuit

The hazards can be minimized by observing the following precautions.

1. Avoid spillage and leakage of water/glycol fluids and defects in the electrical wiring by adhering to workmanship and sound engineering principles.
2. Rigorously clean glycol-contaminated areas (especially silver-clad wiring circuits).
3. Use water/glycol solutions to which are added small amounts of chemical agents (such as benzotriazole) capable of chelating, or immobilizing, the silver ion.

The following conclusions, therefore, are drawn from this study.

1. Water/glycol solutions cannot effectively be evaporated from a region on which spillage has occurred because the ions contained in the corrosion inhibitors of the fluid remain after evaporation of the low-vapor-pressure-producing glycol.
2. The ionizable amine-containing materials remaining after evaporation of water/glycol coolant fluid from equipment surfaces will absorb moisture from the surroundings and thus become progressively more alkaline as the amines are hydrolyzed by the absorbed moisture.

3. Water/glycol solutions with or without inhibitor additions (except for the addition of benzotriazole) produce flammable reactions accompanied by easily detectable radiofrequency radiation upon contacting silver-clad copper wires on which a direct-current potential is impressed.

4. Pure copper, nickel-covered copper, or tin-plated copper wires do not show evidence of chemical reactivity toward water/glycol solutions.

5. Silver-clad copper wiring in circuitry exposed or likely to be exposed to water/glycol coolant should be recognized as a potentially dangerous ignition source.

6. If contamination of silver-wire circuitry occurs, rinsing with distilled water until only a nominal ion pickup is indicated in the rinse water constitutes the recommended decontamination procedure.

7. A silver chelating agent, benzotriazole, when added to water/glycol coolant fluids in concentrations from 2000 to 5000 p/m, completely inhibits reactivity of water/glycol solutions to silver-wire circuitry.

8. An amplitude-modulation receiver covering the commercial broadcast band from 600 to 1400 kilohertz will pick up a constant radiofrequency static noise as the chemical reaction of glycol with silver progresses. Such a receiver, therefore, should serve as a ready detector of incipient trouble in wire circuitry during tests and check-out.

Lyndon B. Johnson Space Center
National Aeronautics and Space Administration
Houston, Texas, October 24, 1975
986-15-31-01-72

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1. Elliot, D. K.: Wet-Wire Fires. Conference on Electrical Insulation, Annual Report. National Research Council Publication 1141, 1964, pp. 124-127.

APPENDIX

CHEMICAL SPOT TEST PROCEDURE

The chemical spot test for ethylene glycol contamination is essentially a test for aldehydes. The test is performed by concentrating the ethylene glycol on a piece of filter paper used as a wiper over the contaminated area and oxidizing the glycol to aldehyde. The preparation of the reagents and the procedure to use for conducting the test are as follows.

PREPARATION OF REAGENTS

1. Ten grams of reagent-grade potassium periodate are dissolved in 200 milliliters of distilled water to give a saturated solution at room temperature. The solution is filtered just before use to remove undissolved potassium periodate.
2. Twenty milliliters of concentrated sulfuric acid are added to 180 milliliters of distilled water to give a 10-percent solution.
3. One gram of rosaniline hydrochloride (basic fushine) is dissolved in approximately 800 milliliters of distilled water. Sulfur dioxide gas is then bubbled through the solution until a pale-orange color is obtained. The solution is then filtered into a 1-liter volumetric flask, and the flask is filled to the mark with distilled water. This solution is allowed to stand overnight before being used as an indicator solution.
4. Concentrated sulfurous acid is prepared by bubbling sulfur dioxide through distilled water. The use of fresh, unsaturated sulfurous acid is mandatory.

PROCEDURE

1. Moisten a piece of filter paper with distilled water. Wipe the moistened filter paper over the area to be tested for water/glycol residue. For a standard, place a drop of water/glycol on the moistened filter paper.
2. Place the filter paper on a clean watchglass and add two or three drops of filtered, saturated potassium periodate solution; then add an identical amount of 10-percent sulfuric acid.
3. Wait 5 minutes to allow oxidation of the glycol to occur.
4. Add five drops of freshly prepared sulfurous acid solution to destroy the excess periodic acid. A faint tan color indicates undestroyed acid. Any undestroyed acid must be eliminated with sulfurous acid before proceeding.

5. Add two or three drops of indicator solution and wait for a color to develop. A positive test for glycol is indicated by a blue or violet color on the filter paper.

It is advisable to run a standard at the same time as the test sample. Because the blue color takes time to develop, running the standard at the same time enables a determination of the time required before a conclusion can be made that the test is negative. Negative results should not be declared until one-half hour has elapsed from the addition of the indicator. A pink color indicates that a mistake has been made and the test must be rerun.